JOURNAL OF MATERIALS SCIENCE 10 (1975) 998–1004

The influence of metal–metal bond energies on the adhesion, hardness, friction and wear of metals

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By calculating the bond energies for various metals, it has been shown that high bond energies herald low magnitudes of self-adhesion in metals. Also, metal-metal bond energies are directly related to the coefficients of friction, hardness and abrasive wear resistance of metals.

1. Introduction

Friction and wear of metals is a subject of great scientific and industrial importance [1-3]. It is of some interest, therefore, to explore the fundamental physico-chemical factors of metals that may determine their friction, wear and related properties such as adhesion and hardness. A great many investigations have been carried out on this subject and, in general, it appears [4] that the phenomenon of adhesion or sticking of metals, which is related to their hardness and friction behaviour, can be correlated with some qualitative features of metals. For example, adhesion of metals has been shown to follow some correlative trends with hardness, elastic modulus, melting point, crystal structure, atomic size, latent heat of vapourization, and surface energy etc. of metals [4-8]. These correlative trends presumably arise because of the influence of the foregoing properties on the bonding in metals [6]. No previous investigations seek to relate the quantitative values of the metal-metal bond energy, b(M–M), to the magnitude of adhesion and related properties of metals. The purpose of the present paper is to explore this point.

2. Some definitions and related matters

The adhesion of a metal may be defined as its tendency to (pressure) bond* to itself. This is a mechanical property which may be studied by a variety of methods (e.g., twist-compression, roll bonding, punch bonding) in which the basic aim is to attain contact between two clean surfaces of the same metal by plastic deformation. One may, of course, investigate the force bonding of one metal to another but the cases of interest in the present paper are only those in which a metal bonds to itself. The coefficient of adhesion is the ratio of the force necessary to break the bond (i.e. the pressure "weld") to the normal loading force with which the samples were initially compressed [4]. The coefficient of friction and the hardness of a metal are parameters whose significance is obvious [1-4]. The hardness of metals may be defined on various scales which have been reviewed by Partington [9].

The metal-metal bond energy, b(M–M), on the surface of a metal is given by [10]:

$$b(\text{M–M}) = \frac{2(\Delta H_s)}{C.N.} \qquad (1)$$

where ΔH_s is the heat of sublimation (i.e. the heat of atomization) of the metal (kcal gat^{-1}) and $C.N.$ is its bulk co-ordination number. By using the values of the highest co-ordination number of the metal [11] and the heats of sublimation [12], one may calculate the b(M–M) values for various metals, as carried out here. The next step is to explore the correlation of b(M–M)

*By the context in which the word "bond" is used, it will be clear to the reader that it denotes two separate things: (i) a pressure "weld" or seal that may be formed when two metal pieces are bonded together by force of compression, i.e., the mechanical bonding, (ii) the bond formed between two atoms of the metal, the so-called metallic bond that holds the metal lattice together and has a characteristic value of bond energy for every metal, i.e. an atomic-electronic property of the metal.

TABLE I

Metal	Median coefficient of adhesion	Coefficient of friction	b(M–M) (kcal)
Pb	3.3	3.5	7.84
Al	1.7	6.0	12.5
Au	1.9	8.0	14.6
Ag	0.8	5.5	11.4
Cu	0.75	18.0	13.5
Pt	0.8	12.8	22.7
Pd	0.65	10	15.0
Ni	0.42	7.5	16.9
Fe	0.30	—	16.6
Ce	0.25	—	16.3
V	0.25	—	30.8
Mo	0.15	—	39.6
W	0.15	—	50.5
Ta	0.30	—	46.7
Ir	0.10	—	26.5
Rh	0.20	—	22.1
Y	1.0	—	16.3
Sn	1.0	—	12.1
In	5.1	—	9.45

Notes: The coefficients of adhesion and friction are from [4] and the b(M–M) values have been calculated as described in the text.

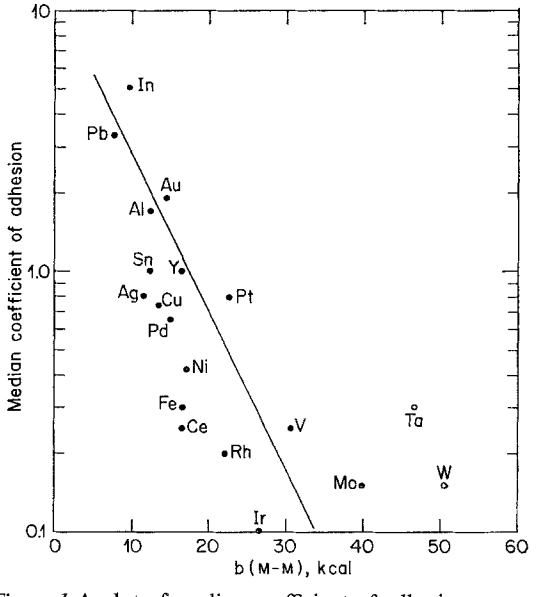

Figure 1 A plot of median coefficient of adhesion versus the b(M–M) values for the shown metals; see Table I for data.

values with the magnitudes of adhesion, friction, hardness and wear of metals, as in the following section.

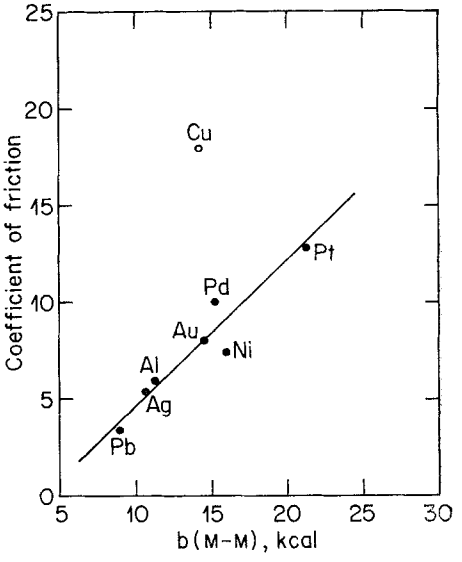

Figure 2 A plot of coefficient of friction versus the b(M–M) values for the shown metals; see Table I for data.

3. Correlation of metal-metal bond energies with adhesion, hardness, friction and wear

In Table I, data on b(M–M) as calculated by Equation 1 together with coefficients of adhesion and friction [4] have been presented. For the fcc, bcc and tetragonal metals, the median coefficient of adhesion [4] decreases with increasing bond energy, although points for Ta and W do not fall near the correlative line drawn in Fig. 1. Metals with hexagonal close-packed structure do not follow this correlation since they have extremely low coefficients of adhesion owing to the peculiarities of their crystal structure as discussed by Sikorski [4]. An interesting aspect of this correlation is that it is approximately valid for three important crystal structures (for the case of Ta and W in Fig. 1, see below) whereas previous correlative trends [4] were applicable to different crystal structures separately.

In Fig. 2, coefficients of friction for eight fcc metals (since these are the only metals for which data have been reported by Sikorski [4]) have been plotted against their b(M–M) values. Except for Cu, a rather good correlation signifying an increase in the cofficient of friction with increasing bond energy is obtained. In all its physico-chemical properties, Cu behaves like Ag and Au; it is surprising, therefore, to note (in Fig. 2)

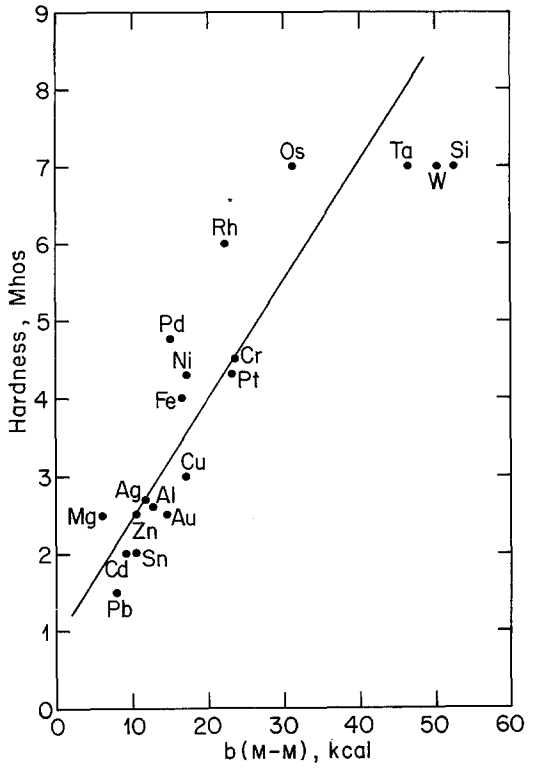

Figure 3 A plot of hardness (mhos scale) [3] of the shown metals against their b(M–M) values.

that the coefficient of friction for Cu is twice as large as that for Ag or Au.

Since coefficients of adhesion and friction are related to the hardness of metals [1-4], it is of interest to explore whether a fundamental physico-chemical property such as the metal-metal bond energy is also related to the hardness of metals. A plot of Mohs hardness [3] against b(M–M) for a large number of metals covering several crystal structures and electronic properties (e.g. sp- as well as d-metals) shows that higher hardness values are associated with higher metal-metal bond energies (Fig. 3). Among the metals for which the data are available, only Mn does not follow the shown correlation (Fig. 3) perhaps because of its rather abnormal (as compared to its position in the periodic table) metallic properties [11, 12]. A similar correlation is obtained when a plot of b(M–M) is examined against the Vickers hardness values (Fig. 4) for the limited number of metals for which these values have been reported by Sikorski [4]. It is clear, therefore, that high b(M–M) values of metals herald high hardness values (Figs. 3 and 4).

TABLE II

Metal	Hardness (kg mm^{-2})	b(M–M) (kcal)
Aluminium	27	12.5
Antimony	58	20.9
Beryllium	150	13.0
Bismuth	7	16.6
Cadmium	22	8.9
Calcium	17	7.3
Cerium	48	16.3
Chromium	125	23.6
Cobalt	125	16.9
Copper	80	13.5
Dysprosium	117	11.9
Erbium	161	11.7
Europium	17	10.7
Gadolinium	97	13.7
Gallium	6.5	25.9
Gold	58	14.6
Hafnium	260	28.0
Holmium	90	11.7
Indium	0.9	9.5
Iridium	350	26.5
Iron	82	16.6
Lanthanum	150	16.7
Lead	4	7.8
Lutetium	118	15.8
Magnesium	46	6.0
Manganese	3300	11.7
Molybdenum	240	39.6
Neodymium	80	12.8
Nickel	210	16.9
Niobium	160	43.1
Osmium	800	31.2
Palladium	110	15.0
Platinum	100	22.7
Plutonium	266	14.3
Potassium	0.04	5.4
Praseodymium	76	14.2
Rhodium	122	22.1
Ruthenium	390	25.8
Samarium	64	8.3
Silver	80	11.4
Sodium	0.07	4.4
Tantalum	88	46.7
Terbium	2	14.9
Thallium	37	7.2
Thorium	53	22.5
Thulium	5.3	9.7
Tin	65	12.1
Titanium	435	18.8
Ytterbium	21	6.7
Yttrium	37	16.7
Zinc	38	10.4
Zirconium	145	24.4

Notes: (1) The hardness values are from [6].
(2) The b(M–M) values have been calculated by Equation 1.

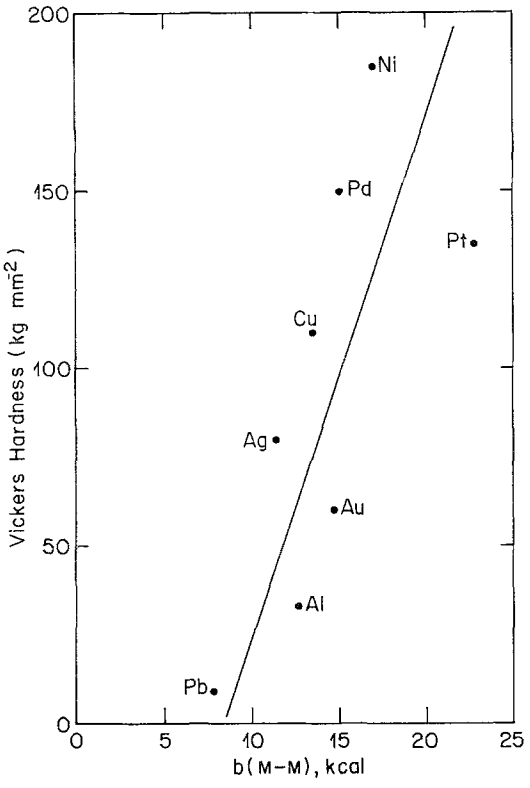

Figure 4 A plot of Vickers hardness [4] against the b(M–M) values of the shown metals.

The most comprehensive and critically selected values of the hardness of the metals appear to have been compiled by Rabinowicz [6] and these values have been collected here in Table II for 52 metals together with their b(M–M) energies. A plot of these data (Fig. 5) gives an "envelope" plot in which for 49 metals, the hardness values (ranging over five decades) tend to increase, roughly, with increasing bond energies, notwithstanding the scatter in this correlation; Mn, Nb and Ta do not fall within the "envelope" for reasons the nature of which is not clear at the present time. In any case, Fig. 5 corroborates the conclusions drawn from Figs. 3 and 4 and is much more general since it includes the complete spectrum of metals, from the extremely soft ones (K, Na, In) to those which are quite hard (e.g. Ti, Ru, Ir, Os etc.).

It seems that the b(M–M) energies also provide a good correlation with the abrasive wear resistance [6, 7] of metals, as shown by the data collected in Table III and plotted in Fig. 6; Be does not follow the shown correlative trend for reasons not clear at the present time. In any case, all other metals show a rather good correlation (Fig. 6).

TABLE III

Metal	Abrasive wear resistance, ϵ	b(M–M) (kcal)
Pb	1.5	7.8
Sn	2.5	12.1
Cd	5.0	8.9
Al	5.3	12.5
Zn	8.0	10.4
Au	8.5	14.6
Cu	9.4	13.5
Ag	10.5	11.4
Pd	13.0	15.0
Zr	14.7	24.4
Pt	15.2	22.7
Ni	17.0	16.9
Co	21.0	16.9
Cr	30.0	23.6
Ti	33.5	18.8
Rh	36.5	22.1
Mo	39.0	39.6
Be	45.0	13.0
W	58.0	50.5

Notes: (1) The abrasive resistance values, ϵ, are from [6]. (2) The b(M–M) values have been calculated by means of Equation 1.

4. Discussion

Although vague references, based on indirect qualitative trends between various parameters, have been made in the literature [4] to the effect that bonding in metals has some bearing on their adhesion, friction, hardness and wear values, a direct examination of the matter by using quantitative values of bond energies in metals has not been done previously.

During the measurement of the coefficient of adhesion, one essentially bonds mechanically two pieces of metal by applying a suitable force. For a given force, such bonding would be expected to be more intimate if the bonds to be ruptured (in the two pieces of metal facing each other before compression) and remade (in the interphasal region created by compression between the two metals) have low energy. When the intimately-united two metals have to be pulled apart subsequently, the force needed to break the "pressure-weld" would be significant, thus giving rise to high coefficients of adhesion for metals with low b(M–M) values. For metals with high b(M–M) values, a given applied pressure would result into a less intimate "weld" simply because the bonds of the mating surfaces

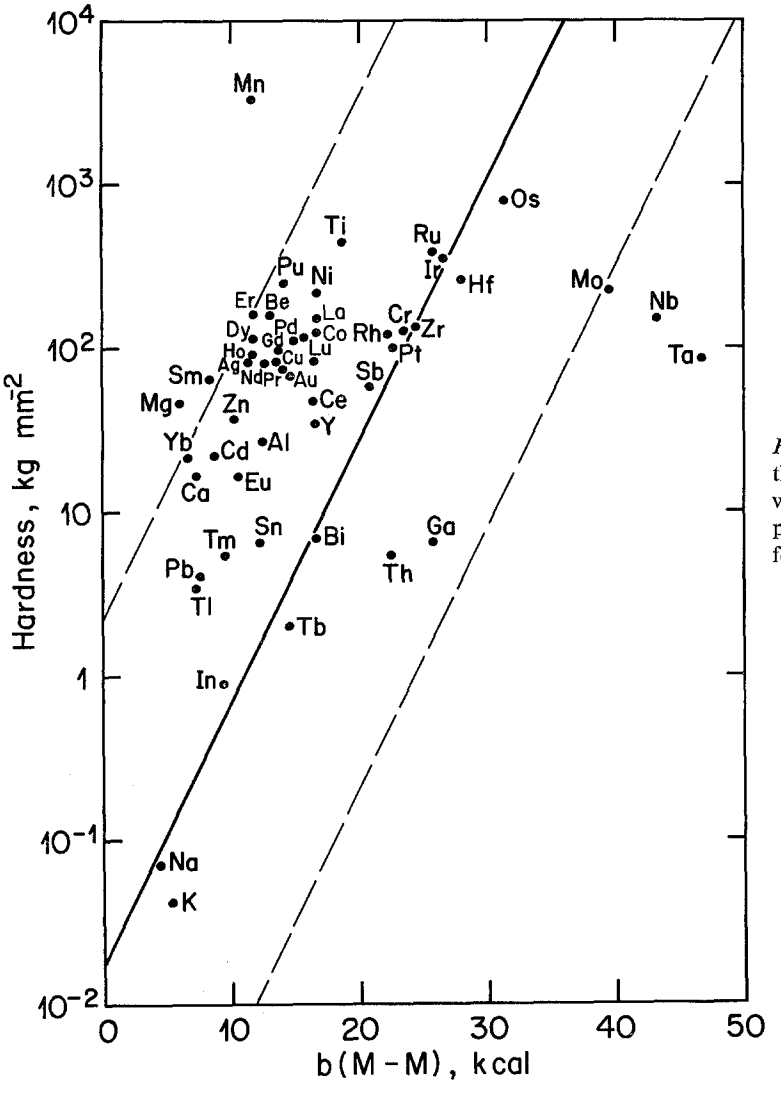

Figure 5 A plot of hardness against the b(M–M) values for all metals for which hardness data have been compiled by Rabinowicz [6]; see Table II for data.

cannot be easily broken, thus excluding the possibility of intimate contact (at the atomic level) and thence interfacial pressure "welding". Lack of an intimate pressure seal during compression leads to a subsequent easy separation of the two metal surfaces; hence, qualitatively, the correlation in Fig. 1. The departures of Ta, W, and to some extent Mo, from the shown trend perhaps arise from the fact that the presence of ever-present oxide on these metals [13, 14] which would tend to give unreliable values of the median coefficient of adhesion and would indeed make it impossible to conduct a valid compression experiment in air. Although Al is also always covered by an oxide, its behaviour in the measurement of surface mechanical properties would be different from that of Ta and W. This is because the oxide on Al is much harder than the underlying metal and is, therefore, easily ruptured thus exposing a relatively clean surface during the experimental measurement of adhesion; this would follow from the "ice on mud" analogy of Bowden and Tabor [1]. In the case of Ta and W, it appears that both the metal and the oxide are fairly hard. This explanation must, however, be regarded as highly speculative and not completely satisfactory.

Since higher b(M–M) values signify that the atoms in the metal are tightly bound and the metal in general is quite hard [8], it is not unexpected that higher b(M–M) values of

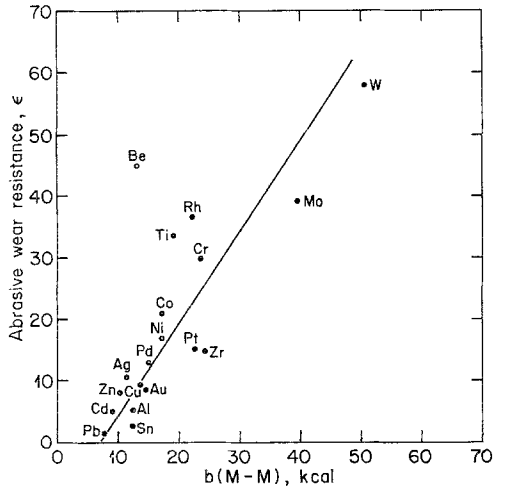

Figure 6 A plot of abrasive wear resistance [6] against the b(M–M) values for the shown metals; see Table III for data.

metals are associated with higher coefficients of friction. For similar reasons, higher b(M–M) values signify harder metals (Figs. 3 to 5).

It is of central interest to examine now the foregoing correlations (Figs. 1 to 6) and the viewpoint in relation to the previous attempts [3-8] to elucidate the fundamental materials properties of metals and their behaviour regarding friction, adhesion, hardness and wear. Giltrow [5] has related the latent heat of sublimation at 25° C (minus the RT term pertaining to the mechanical work necessary to expand atoms, after sublimation, beyond their sphere of influence) to the abration resistance, and thence the hardness [6], of metals. He terms thus corrected latent heat of sublimation as the cohesive energy; this would be true if all metals had the same bulk co-ordination numbers which, of course, they do not [11]. Hence the precise measure of bonding in metals is not the latent heat of sublimation but the actual values of the M–M bond energies as calculated by Equation 1 here. The foregoing argument is somewhat reinforced by the fact that Giltrow does not obtain a linear relationship between his "cohesive energy" and the abrasive wear rate, the latter being linearly related to hardness [6], although he argues that one should obtain a linear relationship between hardness and cohesive energy on theoretical grounds. When one denotes the cohesive energy of a metal by its precise representation in terms of M–M bond energy, as here, one does indeed observe a linear relationship between hardness and cohesive energy (Figs. 3 to 5).

Rabinowicz has chosen surface energy as the central parameter bearing on the mechanical properties of metals [6]. Roughly, surface energy is 1/6 of the heat of sublimation of a metal if the co-ordination number of the metal is 12 [6]: the bond energy calculated by Equation 1 here would thus be approximately equivalent to the surface energy (assuming that both refer to the same temperature, say, 25° C) used by Rabinowicz for metals having body-centred cubic, face-centred cubic, normal close-packed hexagonal and face-centred tetragonal structures, since all these crystal structures have a bulk co-ordination number of 12 [11]. However, for metals having Zn and Cd structure, diamond-type structure, (8-N) complex structure, simple rhombohedral structure and a variety of other complex structures [11], the co-ordination number is less than 12 and the M–M bond energy is not equal to the surface energy. Hence the calculated values of surface energy, as obtained from heats of sublimation, implicitly assume a co-ordination number of 12 for all metals, an assumption not entirely justified. As far as the use of experimental values of the surface energy are concerned, they are usually suspect because of the presence of surface contaminations, chemisorbed layers and oxide films for all metals except perhaps for Au and Pt. In the light of the foregoing remarks, it is clear that it is preferable to use b(M–M) values rather than the surface energy values as the precise index of the bonding in pure metals.

An important feature of Equation 1 is that one obtains the M–M bond energy at the surface of the metal by the use of the bulk properties (heat of sublimation and the co-ordination number) of the metal. One thus deduces the b(M–M) values by relating the bulk and surface parameters of metals and correlates the former, in turn, to the fundamental mechanical properties such as friction, adhesion, hardness and wear of metals.

It is pertinent to point out here that hardness, friction, adhesion and wear are all markedly affected by the presence of impurities. The b(M–M) values calculated by Equation 1 refer, however, to the super-pure metals.

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Received 25 October and accepted 18 December 1974.